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54 ガスバリアー性の優れたポリエステル中空成形体

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明 細 書

1 発明の名称

ガスバリアー性の優れたポリエステル中空成形体

2 特許請求の範囲

1 主たる繰返し単位がエチレンテレフタレートである熱可塑性ポリエステル樹脂からなる中空成形体であつて、該ポリエステル樹脂100重量部当りメタキシリレン系含有ポリアミド樹脂1～100重量部を含有してなることを特徴とするガスバリアー性の優れたポリエステル中空成形体。

2 中空成形体が胴部肉厚部分において少くとも一方向に配向していることを特徴とする特許請求の範囲第1項記載のガスバリアー性の優れたポリエステル中空成形体。

3 発明の詳細な説明

本発明はガスバリアー性に優れたポリエステル中空成形体に関する。さらに詳しくは熱可塑性ポリエステル樹脂とメタキシリレン系含有ポリアミド樹脂との混合からなるガスバリアー性に優れた中空成形体に関するものである。

従来からポリエチレンテレフタレート为主体とする熱可塑性ポリエステル樹脂は、その素材の優れた力学的性質、ガスバリアー性、耐薬品性、保赤性、衛生性などに注目されて各種の容器、フィルム、シートなどに加工され、包装材料として広範に利用されている。特に近年ブロー成形技術とともに二軸延伸吹込成形技術の向上によりびんや缶といった中空容器としての利用も目覚ましいものがある。

然しながらポリエチレンテレフタレート为主体とする熱可塑性ポリエステル樹脂からなる二軸配向した容器として、万全の性能を具備しているわけではなく、特に充填する内容物がガスバリアー性を要求する食品の容器としてはその性能に対するガスバリアー性の不足から不満足であつた。

本発明者は、熱可塑性ポリエステル樹脂がもつ優れた力学的性質を何ら損なわず、また実用的透明性を損なわず、性能に対する遮断性を向上する

本発明者は、熱可塑性ポリエステル樹脂がもつ優れた力学的性質を何ら損なわず、また実用的透明性を損なわず、性能に対する遮断性を向上する

べく鋭意研究を重ね、メタキシリレン基含有ポリアミド樹脂の添加により問題点の解決を見出し、本発明に至った。すなわち、本発明はエチレンテレフタレートの主たる繰返し単位とする熱可塑性ポリエステル樹脂からなる中空成形体であつて、該ポリエステル樹脂100重量部当り、メタキシリレン基含有ポリアミド樹脂1~100重量部を含有してなることを特徴とするガスバリアー性の優れたポリエステル中空成形体である。

本発明でいうエチレンテレフタレートの主たる繰返し単位とする熱可塑性ポリエステル樹脂とは、通常該成分の80モル%以上、好ましくは90モル%以上がテレフタル酸であり、グリコール成分の80モル%、好ましくは90モル%以上がエチレングリコールであるポリエステルを意味し、残部の他の酸成分としてイソフタル酸、ジフェニルエーテル4,4'-ジカルボン酸、ナフタレン1,4-または2,6-ジカルボン酸、アジピン酸、セバシン酸、デカン1,10-ジカルボン酸、ヘキサヒドロテレフタル酸、また他のグリコール成分としてア

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レンジアミンと、炭素数が6~10個の α,ω -脂肪族ジカルボン酸とから生成された構成単位を分子鎖中に少くとも70モル%含有した重合体が挙げられる。

これらの重合体の例としてはポリメタキシリレンアジバミド、ポリメタキシリレンセババミド、ポリメタキシリレンセバミド等のような単独重合体、およびメタキシリレン/パラキシリレンアジバミド共重合体、メタキシリレン/パラキシリレンビバミド共重合体、メタキシリレン/パラキシリレンアゼラミド共重合体等のような共重合体、ならびにこれらの単独重合体または共重合体の成分とヘキサメチレンジアミンのような脂肪族ジアミン、ピペラジンのような脂肪族ジアミン、パラ-ビス-(2-アミノエチル)ベンゼンのような芳香族ジアミン、テレフタル酸のような芳香族ジカルボン酸、 ϵ -カプロラクタムのようなラクタム、 γ -アミノノヘブタン酸のような ω -アミノカルボン酸、パラ-アミノノメル安息香酸のような芳香族アミノカルボン酸等とを共重合した共

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ロビレングリコール、1,4-ブタンジオール、 α -オペンチルグリコール、ジエチレングリコール、シクロヘキサジメタノール、2,2-ビス(4-ヒドロキシフェニル)プロパン、2,2-ビス(4-ヒドロキシエトキシフェニル)プロパンまたはオキシ酸として p -オキシ安息香酸、 p -ヒドロエトキシ安息香酸等を含有するポリエステル樹脂が例示される。また2種以上のポリエステルのブレンドによりエチレンテレフタレートが上記範囲となるブレンドでもよい。

本発明の熱可塑性ポリエステルの固有粘度は0.55以上の値であり、更に好ましくは0.60~1.4である。固有粘度が0.55未満では、容器の前駆成形体であるバリソンを透明な非晶質状態で得ることが困難であるほか得られる容器の機械的強度も不充分である。

また、本発明に使用されるメタキシリレン基含有ポリアミド樹脂は、メタキシリレンジアミン、もしくはメタキシリレンジアミンと全量の30%以下のパラキシリレンジアミンを含む混合キシリ

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重合体等が挙げられる。上記の共重合体においてパラキシリレンジアミンは全キシリレンジアミンに対して30%以下であり、またキシリレンジアミンと脂肪族ジカルボン酸とから生成された構成単位は分子鎖中において少くとも70モル%以上である。

メタキシリレン基含有ポリアミド樹脂(以下S_M樹脂と略記)自体本来は非晶状態では脆いため、相対粘度が通常1.0以上であることが必要であり、好ましくは2.0~4.0である。

従来ガスバリアー性樹脂として公知のエチレン-酢酸ビニル共重合体けん化物はそれ自体が結晶性樹脂であるため、熱可塑性ポリエステル樹脂に添加すると延伸ブロー成形性が損われるほか、得られた中空成形体はバール状に欠陥し実用上透明容器としての機能を有しないし、期待したガスバリアー性も得ることが困難である。

また、スチレン-アクリロニトリル共重合体を添加した場合、そのガラス転移温度(T_g)が低いためポリエステル樹脂に適した延伸温度下で

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は充分延ばされないという欠点を有している。更に非晶性樹脂であつて延伸を施しても配向結晶化を起さないため、残存延伸応力により容易に変形するという欠点も有している。

これらの樹脂に対しSM樹脂自体本来は結晶性樹脂であるが比較的T_gが高いため、熔融状態からの急冷処理により非晶化されやすく、熱可塑性ポリエステル樹脂100重量部当り、SM樹脂100重量部以内、好ましくは80重量部以内の添加では實用性を損なわない透明性を与えると共にそのT_gが熱可塑性ポリエステルのT_gとほぼ等しいことから延伸による配向結晶化が充分に起され、前記高ガスバリアー性樹脂と異なつて熱可塑性ポリエステル樹脂の持つ優れた力学的性質を何ら損なわず、かつ酸素ガス透過性を著しく向上させた中空成形体となる。SM樹脂の特に好ましい配合量はポリエステル樹脂100重量部当り8〜60重量部である。

本発明のガスバリアー性中空成形体を得る方法としては所望濃度の熱可塑性ポリエステル樹脂と

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伸を同時または逐次に行つて吹込成形する方法等が使用できる。

延伸により鋼板肉厚配分は少くとも一方向に配向された中空成形体を得られる。

延伸倍率としては肉厚倍率（軸方向の延伸倍率×径方向の延伸倍率）で2倍以上が好ましく、中には3〜10倍が特に好ましい。前記配合樹脂は、延伸倍率10倍以内を要する。

また、上記配合樹脂から未延伸状のシートを押し出成形した後、延伸により成形した中空成形体や、配合樹脂から押し出または射出成形によつて成形されたパイプを場合により延伸配向させて得られる筒体に嵌を一体化したプラスチック街であつてもよい。

本発明による中空成形体は必要に応じて着色剤、紫外線吸収剤、帯電防止剤、熱酸化劣化防止剤、抗菌剤、滑剤、脱脂剤、上記以外の熱可塑性樹脂等を本発明の目的を損なわない範囲内で含有することができる。

以下、本発明を実施例により詳しく説明する。

なお、本発明で測定した主要特性の測定法を以下

SM樹脂をドライブレンドし、直抄中空体成形機で成形する方法や、所望濃度の熱可塑性ポリエステル樹脂とSM樹脂を押し出機中で熔融混練して混合組成物ペレットを作り該ペレットを中空成形機で成形する方法等が例示される。

また熱可塑性ポリエステル樹脂とSM樹脂の屑状成形物を粉砕機で中空成形機に供給可能な状態に粉砕し、中空成形機で成形する方法も可能である。

中空成形機による成形に関しては、従来のポリエステル樹脂の中空成形と何等異なることなく行なうことができる。例えば一般にダイレクトフローと呼ばれる押し出吹込成形やインジェクションフローと呼ばれる成形で、バリソンを射出成形後充分に冷却しないうちに^正減圧気体により吹込成形する方法や、さらに二軸延伸フロー成形と呼ばれる成形で射出成形または押し出成形により有底開口のバリソンを作製後、延伸フロー装置でバリソンを延伸適温、例えば70〜180℃に加熱し延伸ロッドによる軸方向の延伸と正減気体による径方向の延

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に示す。

(1) ポリエステル樹脂の固有粘度(η_{sp}/C)：フェノール/テトラヒドロフラン=6/4（重量比）混合溶液を用いて30℃で測定した。

(2) ポリアミド樹脂のη_{sp}/C：樹脂1gを9.6重量部減圧100℃に溶解、20℃で測定した相対粘度。

(3) 透明度及びヘーズ：東洋精機社製ヘイズメータBを使用し、JIS-K6714に準じて式より算出した。

$$\text{透明度} = T_2 / T_1 \times 100 (\%)$$

$$\text{ヘーズ} = \frac{T_1 - T_2}{T_1} \left(\frac{T_2}{T_1} \right) \times 100 (\%)$$

T₁：入射光量

T₂：透光側透過量

T₃：設置による散乱光量

T₄：設置とサンプルによる散乱光量

(4) 酸素透過量：東洋MODERN OUTHOLDS社製

酸素透過量測定器OX-TRAN 100Cより、100

cm²×1mm厚の試料の透過量として測定した。

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(54) Polyester Hollow Molding With Excellent Gas Barrier Properties

(21) Japanese Patent Application No. Sho 57[1982]-43429

(22) March 17, 1982

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SPECIFICATION

1. Title of the invention

Polyester Hollow Molding With Excellent Gas Barrier Properties

2. Claims

1. A polyester hollow molding with excellent gas barrier properties, characterized by being a hollow molding composed of thermoplastic polyester resin wherein the primary repeating unit is ethylene terephthalate, and by containing 1-100 parts by weight of a polyamide containing metaxylylene groups with respect to 100 parts by weight of said polyester resin.
2. The polyester hollow molding with excellent gas barrier properties according to Claim 1, characterized in that the hollow molding is oriented in at least one direction in the thin region of the cylinder.

3. Detailed description of the invention

The present invention concerns a hollow polyester molding with excellent gas barrier properties, and in additional detail, concerns a hollow polyester molding with excellent gas barrier properties produced by mixing a thermoplastic polyester resin with a polyamide resin that contains metaxylylene groups.

In the past, thermoplastic polyester resins having polyethylene terephthalate as primary components, have been processed into various types of containers, films and sheets, and have been widely used as packaging materials due to their excellent dynamic properties, gas barrier properties, chemical resistance, storage properties and sanitary properties. In particular, there are materials that are remarkable in terms of use for hollow containers such as bottles or cans due to improvements in biaxial drawing-blow molding technologies that have occurred recently in the blow molding industry.

However, sufficient performance has not been obtained with biaxially oriented containers composed of thermoplastic polyester resins having polyethylene terephthalate as repeating units. In particular, due to its inadequate gas barrier properties with respect to

oxygen, this material is inappropriate for use in food containers with contents that require gas barrier properties.

The inventors of the present invention conducted repeated painstaking investigations concerning the improvement of oxygen-shielding characteristics without any compromise in the excellent dynamic properties or practical transparency of thermoplastic polyester resins, and thus arrived at the present invention by discovering that these problems can be solved by adding a polyamide resin containing metaxylylene groups. Specifically, the present invention is a polyester hollow molding with excellent gas barrier properties, characterized by being a hollow molding composed of thermoplastic polyester resin wherein the primary repeating unit is ethylene terephthalate, and by containing 1-100 parts by weight of a polyamide containing metaxylylene groups with respect to 100 parts by weight of said polyester resin.

The thermoplastic polyester resin having ethylene terephthalate as its primary repeating unit referred to in the present invention denotes a polyester in which terephthalic acid is 80 mol% or more of its acid component, with 90 mol% or more being preferred, and in which ethylene glycol is 80 mol% of its glycol component, with 90 mol% or more being preferred, where the remainder of the acid component is isophthalic acid, diphenyl ether 4,4'-dicarboxylic acid, naphthalene-1,4- or 2,6-dicarboxylic acid, adipic acid, sebacic acid, decane-1,10-dicarboxylic acid or hexahydroterephthalic acid, and the other glycol component is propylene glycol, 1,4-butanediol, neopentyl glycol, diethylene glycol, cyclohexane dimethanol, 2,2-bis(4-hydroxyphenyl)propane or 2,2-bis(4-hydroxyethoxyphenyl)propane, or a polyester resin containing p-oxybenzoic acid or p-hydroethoxybenzoic acid as oxy-acids. In addition, the substance can also be a blend produced by blending two or more types of polyesters so that the ethylene terephthalate is within the aforementioned range.

The intrinsic viscosity of the thermoplastic polyester resin of the present invention is 0.55 or greater, with 0.65-1.4 being additionally desirable. If the intrinsic viscosity is less than 0.55, it will be difficult to obtain a transparent non-crystalline state in the parison used as the preliminary molding for the container, and the mechanical strength of the resulting container will be inadequate.

In addition, examples of the polyamide resin containing metaxylylene groups used in the present invention are polymers that contain at least 70 mol% of structural units in its molecules which are produced from an α,ω -aliphatic dicarboxylic acid with a carbon number of 6-10 and a mixed xylylene diamine containing metaxylylene diamine or metaxylylene diamine and a total of 30% or less of paraxylylene diamine.

Examples of these polymers include polymetaxylylene adipamide, polymetaxylylene sebacamide, polymetaxylylene suberamide and other such simple polymers, metaxylylene-paraxylylene adipamide copolymers, metaxylylene-paraxylylene pimelamide copolymers, metaxylylene-paraxylylene azelamide copolymers and other such copolymers, and copolymers of these individual monomer or copolymer components with hexamethylene diamine or other aliphatic diamines, piperazine and other alicyclic diamines, para-bis-(2-aminoethyl)benzene and other such aromatic diamines, terephthalic acid and other such aromatic dicarboxylic acids, ϵ -caprolactam and other such lactams, γ -aminoheptanoic acid and other such ω -aminocarboxylic acids and para-aminomethylbenzoic acid and other such aromatic aminocarboxylic acids. In the aforementioned copolymers, the amount of paraxylylene diamine is 30% or less with respect to the total amount of xylylene diamine, and the amount of structural units generated from the xylylene diamine and aliphatic dicarboxylic acid is 70 mol% or greater in the molecular chains.

The metaxylylene group-containing polyamide resin (referred to below as "SM resin") is itself intrinsically brittle when in its non-crystalline form, and so the relative viscosity ordinarily must be 1.5 or greater, with 2.0-4.0 being preferred.

Ethylene-vinyl [illegible; possibly "acetate"] copolymer saponification products that are well known in their use as conventional gas barrier resins are themselves crystalline resins, and so when added to thermoplastic polyester resin, their drawing and blow-molding properties are lost, or the resulting hollow molding will [illegible] into a ball form. The material thus will not have practical functionality as a transparent container, or it will be difficult to obtain the desired gas barrier properties.

Moreover, when styrene-acrylonitrile copolymer is added, the glass transition temperature (T_g) will be high, and there is thus the disadvantage that sufficient drawing will not occur under drawing temperatures that are appropriate for the polyester resin.

Moreover, when drawing is carried out, oriented crystallization will not occur because the material is a non-crystalline resin, which is disadvantageous in that the container will be modified due to residual drawing strain.

The SM resin itself has an intrinsically higher T_g relative to these resins because it is a crystalline resin, and is readily rendered non-crystalline by a quenching treatment from the melted state. When the added amount of SM resin is within 100 parts by weight with respect to 100 parts by weight of the thermoplastic polyester resin, with 60 parts by weight being preferred, oriented crystallization will be adequately induced by drawing without changing its practical transparency, because the T_g thereof will be nearly equivalent to the T_g of the thermoplastic polyester resin. As a result, a hollow molding with excellent oxygen gas barrier properties will be obtained without any compromise of the excellent dynamic properties of the thermoplastic polyester resin, in contrast to the aforementioned resins with good gas barrier properties. A particularly desirable blending ratio for the SM resin is 5-60 parts by weight with respect to 100 parts by weight of the polyester resin.

An example of a method for obtaining the hollow molding with good gas barrier properties of the present invention is a method wherein the thermoplastic polyester resin and SM resin are dry blended at the desired concentrations, and the material is directly molded with a molding device for hollow moldings, or a method wherein the thermoplastic polyester resin and SM resin are fused and kneaded in an extruder at the desired concentrations to produce a mixed composition blend, whereupon said blend is molded using a molding device for hollow moldings.

Moreover, a method can also be used wherein a layer-form molding composed of thermoplastic polyester resin and SM resin is milled with a mill into a form whereby it can be fed to the hollow molding device, whereupon molding is performed with the hollow molding device.

In regard to molding carried out with the hollow molding device, molding can be carried out in exactly the same manner as with conventional polyester resin hollow moldings. For example, injection-blow molding can be carried out which is referred to as direct blowing, or, in a method known as injection blowing, a parison can be produced by injection molding, and can then be subjected to blow molding with compressed gas while

the material has not sufficiently cooled. Moreover, molding can be carried out by a method referred to as biaxial drawing/blow molding, or a blow molding method may be used wherein a parison with a bottom and an opening is produced by injection molding, whereupon the temperature of the parison is adjusted in a drawing/blowing apparatus to a temperature appropriate for drawing, for example 70-150°C, and axial drawing with a drawing rod and circumferential drawing with compressed air are carried out simultaneously, or in succession.

A hollow molding is thus obtained wherein the thin region of the cylinder produced by drawing is oriented in at least one direction.

In terms of drawing expansion factor, it is preferable for the surface area expansion ratio (axial drawing expansion ratio x transverse drawing expansion ratio) to be 2 or greater, with 3-15 being preferred. The final thickness in the thin region of the cylinder is ordinarily 0.1 mm or greater, with 0.15 mm or greater being preferred, and 0.2-1 mm being additionally desirable.

In addition, a plastic can also be formed by integrating an [illegible] with a hollow molding formed by deep drawing an undrawn sheet after extrusion molding from the aforementioned mixed resin, or with a cylinder obtained by drawing and orienting, when necessary, a pipe that is produced by injection molding or extrusion molding from the mixed resin.

The hollow molding of the present invention can also contain, as necessary, colorants, ultraviolet absorbers, antistatic agents, thermal oxidation inhibitors, antimicrobial agents, lubricants, nucleators, and thermoplastic resins other than those mentioned above, in ranges in which the objectives of the present invention are not compromised.

The present invention is described in additional detail below using working examples. The measurement methods for the main characteristics measured in the present invention are shown below.

(1) Intrinsic viscosity (η) of the polyester resin:

Measured at 30°C using a mixed solvent of phenol/tetrachloroethane = 6:4 (weight ratio).

(2) η_{rel} of the polyamide resin:

1 g of resin is dissolved in 100 mL of 96 wt% sulfuric acid, and the relative viscosity is measured at 25°C.

(3) Transparency and haze:

Calculated by a formula according to JIS-K6714 using a Toyo Seiki Hazemeter S [illegible; possibly "8"].

Transparency: $T_2/T_1 \times 100$ (%)

Haze: $(T_4 - T_3(T_2/T_1))/T_2 \times 100$ (%)

T_1 : Incident light quantity.

T_2 : Total light quantity transmitted.

T_3 : Quantity of light scattered by the device.

T_4 : Quantity of light scattered by the device and sample.

(4) Oxygen permeability:

Measured at 20°C with the oxygen permeability measurement device OX-THAN 100, manufactured by U.S. Modern Controls, and expressed as the permeability per [illegible] cc/bottle. (cc/container-24 h-atm)

(5) Tensile characteristics:

Strips with widths of 10 mm were used, and the yield strength, and break elongation were measured under conditions of a chuck separation of 50 mm and a pull rate of 50 mm/min (23°C) with a Toyo Baldwin Tensilon.

Working Examples 1-5 and comparative example

A Polyethylene terephthalate ("PET") with an (η) value of 0.72 was used as the polyester resin, and a polymetaxylylene adipamide ("SM resin") with a η_{rel} of 2.2 was used as the polyamide resin containing metaxylylene groups. A bottomed parison with an outer diameter of 25 mm, a length of 130 mm and a thickness of 4 mm was molded under the molding conditions shown in Table I using an M-100 injection molder manufactured by Meiki Seisakujo

The parison was then heated by fitting the open end of the parison on a parison fitting provided with an automatic drive device, and rotating the parison in an oven with an infrared heater to heat the parison to a surface temperature of 110°C. Subsequently, the parison was transferred into a blow mold, and blow molding was carried out under

conditions comprising a drawing rod rotation rate of 22 cm/sec and a compressed air pressure of 20 kg/cm². A beer bottle shaped hollow container was thus obtained with a total length of 265 mm, a cylinder outer diameter of 80 mm and an inner volume of 1000 mL. The performance of these containers is shown in Table 2.

Table 1

	Working Examples 1, 2 Comparative example	Working Example 3	Working Examples 4, 5
Cylinder temperature (°C) (from hopper side)	250 x 285 x 285	250 x 285 x 285	250 x 285 x 285
Injection pressure (kg/cm ²) (gage pressure)	27	28	30
Mold temperature (°C)	15	16	15
Injection time (sec)	15	10	10
Cooling time (sec)	12	10	17

Table 2

	PET resin parts by weight	SM resin parts by weight	Tensile yield strength kg/cm ²	Transparency %	Haze %	Oxygen permeability cc/bottle·24h·atm
Working Example 1	95	5	1092	77	19	0.34
Working Example 2	90	10	1108	70	28	0.25
Working Example 3	80	20	1123	63	40	0.20
Working Example 4	70	30	1109	56	47	0.17
Working Example 5	50	50	1101	45	61	0.11
Comparative example	100	0	1106	90	3.8	0.55

The containers obtained in these working examples had dramatically improved oxygen gas barrier properties in comparison to the conventional polyethylene terephthalate container shown in the comparative example, with no detrimental effects on dynamic properties and no loss in practical transparency. The resulting containers can also be coated with water-resistant or scratch-resistant coatings as desired.